MOLECULAR MOTION IN FLUIDS AND INTERNAL DISPERSION AND ABSORPTION OF ELASTIC AND OPTICAL WAVES

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ABSTRACT. A theory has been worked out on the basis of molecular motion to determine the absorption and internal dispersion of optical and elastic waves. The present available data on the supersonic absorption have been explained. A general broadening of the lines in the diffraction spectra obtained by the wave field grating has been noted and satisfactorily explained on the basis of a range of elastic wave velocity. The broadening of the spectral lines obtained with the help of a plane diffraction grating has also been noted and attributed to the effect of molecular motion in the liquids.

INTRODUCTION

The velocity of the elastic waves is determined by the relation,

$$V^2 = d\rho/dp = \frac{1}{\rho\beta} \qquad \ldots (1)$$

where, β is the adiabatic compressibility. In the case of a gaseous medium, the relation works out in the simple, well known form,

$$V^2 = \gamma p/\rho \qquad \ldots (1a)$$

where, γ is the ratio of the specific heats. These relations bring out the important and verified characteristic property that the sound velocity is independent of the frequency of waves, unlike the optical waves. The above relations have been obtained without any associated relation for the absorption of the waves, as is usual for the optical case. A relation determining the absorption was given by Stokes (1845), on the basis of the equation of motion of a viscous medium, in the form,

$$\alpha/\nu^2 = \frac{8\pi^2\eta}{3\rho V^3} \qquad \ldots (2)$$

where, α is the absorption coefficent per unit length, η the viscosity coefficient and ν is the frequency of the wave motion. The method of procedure, however, does not give a corresponding relation for the velocity of the waves. The relation indicates that α should be proportional to ν^2 or that α/ν^2 should be a constant for different frequencies. The experimental findings are that α/ν^2 is independent of frequency for a medium, but the magnitude of the constant is generally a multiple of the Stokes' constant. The experimental values of this Stokes' constant multiplier, M, varies from 1 to the

order of 1000 in the case of different substances. No justifiable explanation of this has been forthcoming, although attempts to explain it by the principle of relaxation mechanism have been made by different workers on the lines of Dutta and Ghose (1937-38, Kneser, 1938). Further, it has been experimentally observed (Rapuano, 1947; Biquard, 1935; Willard, 1941) that liquid carbon-bisulphide, which has the Stokes muliplier as 1500 in the region upto 1 megacycle per second has a drop in the amount of α/ν^2 by 1/5th, in the region of 100 megacycles per second. In the case of acetic acid (Pikerton 1948), the value of α/ν^2 shows a rapid increase with decreasing frequency, the magnitude being about 3000×10^{-17} c.g.s. units in the region of a few megacycles. The Stokes constant would be only of the order of a few units of 10^{-17} c.g.s. units.

An important clue to the explanation of the whole phenomenon is the associated breadth of the spectral lines obtained by the method of Debye and Sears (1932), where diffraction spectrum is produced by the elastic wave field grating. It might have been noticed by all workes in the line that, whereas, water with the Stokes multiplier as 3, has very sharp spectral lines, CS_2, with the Stokes multiplier as 1500 has very diffuse and broad lines. Benzene, with a Stokes multiplier of about 100, has a breadth of the spectral lines in between them. One possible cause of this spreading of the spectral lines might be a range of variation of the velocity of the elastic waves and this would mean that a liquid with a large absorption coefficient or rather with a large Stokes multiplier has a large range of variation of the wave velocity. Such a varied range of velocities, in the case of substances, with different magnitudes of the Stokes multiplier has been obtained below on theoretical grounds. The spreading of the velocity may be termed as internal dispersion.

In order to substantiate internal dispersion and explain absorption, relations have been obtained for the elastic wave velocity and the absorption coefficient, on the basis of molecular motion, very similarly to the procedure adopted for the treatment of the optical wave velocity and absorption, on the basis of electronic motion.

THEORETICAL PROCEDURE FOR ELASTIC WAVES

The usual optical relation,

$$D = KE$$

where, D, is the electric displacement, E is the electric field, and K, the dielectric constant, is determine by the relation $K = C^2/V^2$, has a corresponding relation in elastic waves, when we set equation (1) in the form,

$$d\rho/\rho = K dp/p \qquad \ldots (3)$$

Here $d\rho/\rho$ and dp/p denote the relative displacement and relative pressure change, and $K = \frac{p/\rho}{V^2}$, may be termed as the dielastic constant.

When $K=1$, we have $V^2=p/\rho$, in the ideal conditions when relative displacement would be equal to the relative pressure change. In optics under such ideal conditions, one has $V^2=C^2$, determining the velocity of the light in vacuum.

A convenient method of finding the velocity of light in ordinary matter is to consider the polarisation in the medium, due to electric field and set up an equation for the electric displacement in terms of the incident field and the polarisation. Thus, we take up the optical relation,

$$D=KE=E+4\pi P$$

such that $E+4\pi P=KE$, is the effective field in the medium to have an equivalent displacement. When we are able to express the polarisation in terms of the electric field, such that, $D=E(1+\delta)$, we have solved the optical problem, in as much as we have equated K to $1+\delta$, and the velocity of the light waves becomes determined.

In the relation (3), namely, $d\rho/\rho=Kdp/p$

the quantiy Kdp is the modified pressure change, which has an equivalent relative displacement. We may consider the nett effective dp, in producing an eqivalent displacement, as the sum of the actual pressure change dp together with a polarisation pressure due to dp, similarly as in the case of light. This enables one to set,

$$Kdp=dp+\text{polarisation pressure due to } dp, : \quad \ldots (4)$$

The velocity of the elastic waves would be obtainable from the value of K, when the polarisation pressure due to dp could be explicitly expressed in terms of measurable quantities, with dp as a factor.

The polarisation pressure could be obtained, when we are able to write the complete equation of motion in terms of molecular motion. This would, naturally, involve the polarisation pressure as one of the terms in the equation of motion. In order to proceed to write the equation of motion, we consider a layer of the fluid with an area of unit cross section. We consider the extra force per unit area dp, acting on any surface inside the medium, as equivalent to the extra force on the N molecules attached per unit area, each with a mass 'm', together with a force of excitation of the molecules to different states, depending on the respective probability factors and some preventive or polarising force per unit area. The polarisation may be considered to be caused by the changes in the condition of stress of the medium with time. If we regard the displacement due to dp, in any direction, as ξ, we may set the equation of motion in the form,

$$dp-\text{polarisation pressure}-\text{excitation loss}=N.m.\ddot{\xi}, \quad \ldots (5)$$

We have not considered, yet, the force of friction and the force of restitution acting on the molecules. When these are also taken into account, we obtain the complete equation of motion.

The extra force on unit area due to the polarisation, is produced by the time rate of change of stress at a point, and acts only during a change of the conditions of stress and vanishes when the change in the stress condition is made to disappear. As is well known, the stress components in a fluid medium is measured in terms of the time rate of change of displacements of the elements and not in terms of the displacements as for solids. This leads one to presume that the polarisation pressure contribution of dp should be considered as proportional to the impressed acceleration of the particles. Regarding the polarisation force, it is also evidently proportional to the total number of particles per c.c., and to a polarisation coefficient, One may thus set the polarisation force per unit area as $P(Nm)\ddot{\xi}$. Similarly, the loss of pressure due to excitation is expressible in the form $-\alpha N.m\ddot{\xi}$. We have here α as the excitation coefficient and $P(Nm)$ involves the polarisation coefficient and the number of molecules per c.c.. One has also to take into account the force of restitution and the force of resistance acting on the particle. These forces acting on the molecules are expected to have a large or small range of variation depending on the structural character of the molecules involved. These forces will act in a direction opposite to the direction of polarisation, helping the particles to return to the status quo, *i.e.*, of motion. Further, the force of restitution will involve the same function of ξ as the polarisation and the force of resistance will contain the time rate of change of the function of ξ involved in polarisation. One may, thus, set the complete equation of motion in the form,

$$\{dp-P(N, m)\ddot{\xi}-\alpha N.\ m\ddot{\xi}\}/N=m(\ddot{\xi}-f\ddot{\xi}-g\frac{d}{dt}\ddot{\xi})$$

$$\text{or}\quad (dp+Nmf\ddot{\xi}+Nmg\frac{d}{dt}\ddot{\xi})-P(N, m)\ddot{\xi}=Nm\ddot{\xi}(1+\alpha) \qquad \ldots\ (6)$$

where f and g are the coefficients of restitution and friction and will have a range. Since, further, $P(N, m)$ is determined by the number of molecules per c.c. and by a polarisation coefficient, one may set

$$P(N, m)=N.m.q$$

for a gaseous medium and for any other medium, with a density ratio compared to the particular gaseous state as R, one has the general relation

$$P(N, m)=R.N.m.q. \qquad \ldots\ (7)$$

For a particular gaseous state q involves constants specifying the number of molecules and their masses and a polarisation constant. The polarisation constant is expected to be dependent upon the temperature and to fix upon R, one has to take the different states under similar conditions of temperature. The equation of motion (6) may, then, be expressed in the form,

$$(dp + Nmf\ddot{\xi} + Nmg\frac{d}{dt}\ddot{\xi}) - RqNm\ddot{\xi} = Nm\ddot{\xi}(1+\alpha) \qquad \ldots \quad (6a)$$

One may determine the unknown polarising coefficient q by studying the problem from another point of view. Let us consider the gaseous state, with R as unity. The total impressed energy will give rise to the energy of motion and excitation together with the energy of polarisation in the form of fluid strains. The polarisation part is a sort of conservation or storing up of energy that comes into existence only when there is a strain variation. When the energy is supplied at constant volume, the strain energy part remains unchanged and the polarisation term vanishes. The input energy, $C_v dT$, would be measured in terms of energy of motion and excitation only. Gradually, as the associated strain variation is established, the input energy, $C_p dT$. would be measured in terms of energy of motion and excitation, as also by the polarisation energy. Thus we have the right hand side of the above equation (6a), as a measure of $C_v dT$, the term in the parenthesis as a measure of $C_p dT$, and the polarisation term $qNm\ddot{\xi}$ as a measure of $(C_p - C_v)\, dT$. This is in accordance with the accepted idea, that the specific heat at constant volume is a measure of the energy of motion $C_a dT$, together with the energy of excitation $C_i dT$. Indeed, it is the frequency dependence of $C_i dT$, that gives rise to the principle of relaxation phenomenon. For our present treatment, we disregard the consideration of the frequency dependence of the specific heat at constant volume, that is, we consider α as frequency independent. Since $qNm\ddot{\xi}$ is a measure of the energy difference $(C_p - C_v)dT$, the above relation immediately indicates that when $q = 1 + \alpha$, we would have, $C_p = 2C_v$. This gives us,

$$q = (1+\alpha)(\gamma - 1),$$

where, γ, is the ratio of the specific heats. We have thus, determined the unknown polarising coefficient q, at any temperature, in terms of γ, the ratio of the specific heats of a particular gaseous state of the matter concerned, even when we are treating the case of a liquid state. We have, then, the polarising pressure in the form,

$$-P(N, m)\ddot{\xi} = -RNm(1+\alpha)(\gamma - 1)\ddot{\xi},$$

and the equation of motion becomes,

$$dp = Nm(1+\alpha)\{1 + R(\gamma - 1)\}\ddot{\xi} - Nmf\ddot{\xi} - Nmg\frac{d}{dt}\ddot{\xi}$$

With a periodic change of pressure $dp = dp_0 . e^{i\omega t}$, and the associated displacement as $\xi = ae^{i(\omega t - \varphi)}$, one obtains, immediately,

$$\xi = -\frac{dp/Nm}{(1+\alpha)\{1 + R(\gamma - 1)\}\omega^2 - f\omega^2 - ig\omega^3}$$

and thus, one may set the polarisation pressure,

$$-P(N, m)\ddot{\xi}=R(1+\alpha)(\gamma-1).N.m.\omega^2\xi.$$

$$=-\frac{R(\gamma-1)(1+\alpha)dp}{(1+\alpha)\{1+R(\gamma-1)\}-f-ig\omega} \quad \ldots (8)$$

If we consider n as the elastic index of refraction and k as the coefficient of absorption per unit wavelength, we have, in view of relation (4), the di-elastic constant K as,

$$K=(n-ik)^2=\left[1-\frac{R(\gamma-1)(1+\alpha)}{(1+\alpha)\{1+R(\gamma-1)\}-f-ig\omega}\right] \quad \ldots (9)$$

The real part of the di-elastic constant would be given by,

$$n^2-k^2\simeq n^2=\frac{p/\rho}{V^2}=1-\frac{R(\gamma-1)(1+\alpha)[(1+\alpha)\{1+R(\gamma-1)\}-f]}{[(1+\alpha)\{1+R(\gamma-1)\}-f]^2+g^2\omega^2}$$

$$=1-\frac{R(\gamma-1)(1+\alpha)}{(1+\alpha)\{1+R(\gamma-1)\}-f+g'^2\omega^2}$$

where,

$$g'^2=g^2/[(1+\alpha)\{1+R(\gamma-1)\}-f] \quad \ldots (10)$$

For liquids, we would have the approximate relation,

$$g'^2=g^2/(1+\alpha)R(\gamma-1) \quad \ldots (10a)$$

Thus, we have,

$$\frac{p/\rho}{V^2}=\frac{(1+\alpha)-f+g'^2\omega^2}{(1+\alpha)-f+g'^2\omega^2+(1+\alpha)R(\gamma-1)} \quad \ldots (11a)$$

or

$$V^2=\frac{p}{\rho}\left\{1+\frac{R(\gamma-1)}{1-F+G^2\omega^2}\right\} \quad \ldots (11)$$

where,

$$\left.\begin{aligned} &F=f/(1+\alpha), \\ &G^2=g'^2/(1+\alpha)=g^2/(1+\alpha)^2R(\gamma-1)=g''^2/R(\gamma-1) \\ &\text{with} \quad G=g''/(1+\alpha) \end{aligned}\right\} \quad \ldots (12)$$

The imaginary part of the di-elastic constant K determines the absorption coefficient k. We have by equating the imaginary parts, in relation (9).

$$2nk=\frac{R(\gamma-1)(1+\alpha)g\omega}{[(1+\alpha)\{1+R(\gamma-1)\}-f]^2+g^2\omega^2}.$$

Utilising the relations (11*a*) and (10) we have

$$[(1+\alpha)\{1+R(\gamma-1)\}-f]^2+g^2\omega^2=\rho\frac{V^2}{p}\left\{(1+\alpha)-f+g'^2\omega^2\right\}$$

$$\times[(1+\alpha)\{1+R(\gamma-1)\}-f]$$

Thus, we obtain,

$$2nk=\frac{pR(\gamma-1)(1+\alpha)g\omega}{\rho V^2\{(1+\alpha)-f+g'^2\omega^2\}[(1+\alpha)\{1+R(\gamma-1)\}-f]} \quad \ldots (13)$$

For a liquid, neglecting 1 and f, compared to $R(\gamma-1)$, the relation reduces to,

$$2nk=\frac{\rho g\omega}{\rho V^2\{(1+a)-f+g'^2\omega^2\}} \quad \ldots \quad (13a)$$

Thus the absorption coefficient k per unit wave length would be given by,

$$k=\frac{2\pi\rho g''\nu}{2n\rho V^2(1-F+G^2\omega^2)} \quad \ldots \quad (14)$$

where the coefficients F, G, g'', etc., are defined by the relation (12). The absorption coefficient per unit distance, would be determinable from,

$$\alpha/\nu^2=\frac{k}{V\nu}=\frac{\pi\rho g}{n\rho V^3(1-F+G^2\omega^2)} \quad \ldots \quad (15)$$

ANALYSIS OF THE THEORY AND THE EXPERIMENTAL DATA

When we neglect the effect of the small quantities F and G the velocity equation (11), immediately reduces to the gas velocity equation (1a). It also gives us the so far undeterminable liquid pressure, by the approximate relation,

$$\rho=\frac{\rho V^2}{R(\gamma-1)}$$

In the case of liquids, with V^2 of the order of 10^{10}, $R(\gamma-1)$ of the order of 3.10^2, the pressure comes out of the order of 30 atmospheres, and n the elastic index of refraction in liquids about 5.10^{-2}. For gases, the elastic index of refraction would be given by,

$$n=\left(\frac{\rho}{\rho V^2}\right)^{1/2}=(1/\gamma)^{\frac{1}{2}}\simeq 8\times 10^{-1}$$

When we take the small quantities F and G into account and take note, that both of them are likely to have a large or small range of values, about the mean, depending upon the structure and constitution of the molecules, the Eq. (11) indicates that the velocity will have a range about its mean value, which may be termed as internal dispersion.

There is no sense, however, in absorption coefficient having a range of values. It will be experimentally determined by its maximum value only. The observed intensity will always be the lowest possible intensity, as reduced by the molecules moving under the largest value of the force of friction.

The absorption equation (15) is in complete accord with a constant value of α/ν^2 for smaller values of ω, and is very similar to the Stokes relation (2). On comparing these two equations, we may write,

$$\alpha/\nu^2=\frac{8\pi^2\eta}{3\rho V^3}=\frac{\pi\rho g''}{n\rho V^3}$$

Thus the coefficient g'' is determinable by the relation,

$$g'' = \frac{8\pi n}{3p} \cdot \eta \qquad \ldots \quad (16)$$

As the viscosity coefficient, η, has only an average value, the value of g'', thus determined would give us only the average value. The experimental value of α/ν^2 will, however, give us the maximum value of g'', and one may consider that the range of extension of g'' from its mean value is given by the Stokes multiplier M. This would be more apparent when we consider the structure of different molecules and their M values, as discussed in detail in experimental paper on 'Internal dispersion', which follows.

It is possible, now, to calculate the mean value g'', from relation (16) above. For a liquid like CS_2 the value of g'' comes out about 3.10^{-11}. The value of g''_{max} would be fixed up by $M.g''$, where M is the Stokes multiplier. With a Stokes multiplier of 1500 for CS_2 (Pinkerton, 1949), one gets its $g_{max} = 4.5 \times 10^{-8}$, and the corresponding value of G is given by the relation,

$$G_{max} = \frac{g''_{max}}{[R(\gamma - 1)]^{1/2}} = 3 \times 10^{-9}$$

The relation (15), with such a value of G gives the fall of α/ν^2 to 1/5th its value, when the frequency changes from 10^6 to 10^8 c.p.s. It is, thus, in exact agreement with the experimental results of Rapuano, (1947) and others, that has been pointed out in the introduction.

Acetic acid would have a calculated mean g'' value and the Stokes α/ν^2 value, of the same order as that for CS_2. The experimental value (Pinkerton, 1948 and Bazulin, 1936) of α/ν^2, however, shows a very rapid increase with decreasing frequency, and at about 10^6 c.p.s., it becomes nearly 1000 times as large as Stokes' calculated value. It may be easily calculated with the help of relation (15), that with a Stokes multiplier of the order of 10^4, which, from experimental data to date, is not at all an unlikely value, the characteristics of the α/ν^2 variation with ν, obtained experimentally, would, be fully explained. A small constant tail portion of the experimental results, however, remains unexplained. This may be reasonably attributed to the relaxation mechanism, having a maximum absorption, somewhere further up, in the high frequency region. Further, it gives one immediately that the usual character of the constant α/ν^2 value, would be obtained, on the low frequency side, near about 5.10^4 cycles per second. The experiment is worth trying.

The idea that the Stokes multiplier is to be regarded as giving the range of variability of g or G is nicely corroborated from the internal dispersion of spectral lines, obtained by the Debye and Sears (1932) diffraction method. A detail treatment of the subject is made in the experimental paper, that will follow. It is clear, however, from the velocity relation (11), that an internal dispersion or a broadening of the diffraction spectra lines, would be very large for a substance like CS_2, with an M value of 1500 and least for a liquid

like castor oil (Hunter, 1941, Pinkerton, 1949), with an M value of one only, although the magnitude of observed α/ν^2 is nearly the same in the two cases. The experimental results on the width of the diffraction spectra lines, completely support this point of view, and one obtains the sharpest line with pure castor oil, whose breadth is actually fixed up by the Doppler broadening of the source only. With the other liquids, the Stokes multipliers and the spectral line widths are in good correspondence.

Further, even the large M value of CS_2, in association with the mean G would not give the observed internal dispersion, at low frequencies, of the order of one or two megacycles, when it is calculated by the velocity relation (11). One has to regard that F along with G would be of a variable character, determined by the Stokes multiplier M, and this is quite reasonable to expect.

It may be pointed out, however, that as the mean value of G is of the order of 10^{-12}, the dispersion of the mean velocity would not be obtained until the frequency region of 10^{19} to 10^{11} c.p.s., is reached. The experimental results on mean dispersion, till now, is generally in agreement with this outcome of the theory.

INTERNAL DISPERSION OF OPTICAL WAVES

The molecular motion in a fluid medium, with its associated variable forces of restitution and friction would also give rise to an internal dispersion of optical waves and thus, also, the associated broadening of the spectral lines obtainable, say, by a plane glass diffraction grating. Such an effect, with greater broadening of spectral lines in liquids with large M values, have been observed and is being reported to in a separate paper. The basic relations, in consideration of the molecular motion, will be obtained in the following :

Any molecule, in view of its relative position with regard to its neighbours, will possess an instantaneous strong dipole moment p, say. The polarisation of the liquid, due to any further rotation of the dipole molecule, caused by any incident electric field, will give rise to a contribution in the dielectric constant and thus, will have an effect on the optical wave velocity. If we consider the electric field in the direction of x, the electrical polarisation in the same direction, caused by the rotation of the molecule, would be given by,

$$P_{m,x}=\Sigma N p_x'=\Sigma N p_y \varphi \qquad \ldots \quad (17)$$

were, p_x' is the projection of the initial electric moment component p_y on the x axis, after it has been rotated by the electric field through any small angle φ. N here denotes the number of molecules per cubic centimetre. This gives us the additional polarisation, besides the usual electronic polarisation, which plays the major part.

The equation of motion of the molecule would be obtained by taking the z-component of the torque on the molecule. In accordance with the usual form of the torque relation, we may write,

$$\left[\vec{E'}, \vec{p}\right]_z = I\varphi + IG\varphi + IF_0^2\varphi \qquad \ldots \quad (18)$$

Here φ is the angle of rotation, G and F_0^2 determine the frictional force and the force of restitution, I, is the moment of inertia of the molecule, and $\vec{E'}$ is the total electric field acting on the molecule. The total electric field in the liquid would be given by the relation,

$$E_x' = E_x + \frac{4\pi}{3} P_e + \frac{4\pi}{3} P_m \qquad \ldots \quad (19)$$

where P_e and P_m stand for the electronic and molecular polarisation parts. The electronic polarisation part in liquids is known and we may set, (Slater and Frank, 1933)

$$\frac{4\pi}{3} P_e = E\frac{4\pi}{3} \frac{\Sigma N_k l^2/m}{f_k^2 - \omega^2 + 2\omega g} = Ef(\epsilon) \qquad \ldots \quad (20)$$

where ϵ and m denote the electronic charge and the mass, ω specifies the incident frequency. $f_k^2 = f_k^2 - \frac{4\pi}{3}\Sigma N_k \epsilon^2/m$, with f_k^2 giving the coefficient of of restitution and g the coefficient of friction acting on the electron. Utilising the two polarisation expressions (17) and (20) and considering the incident electric field polarised in the x direction, we may put the equation of motion in the form,

$$E_x' p_y = I\ddot{\varphi} + IG\dot{\varphi} + IF_0^2\varphi.$$

or
$$\{E_x(1 + f(\epsilon)) + \Sigma 4\pi/3\ Np_y\varphi\}p_y = I\ddot{\varphi} + IG\dot{\varphi} + IF_0^2\varphi \qquad \ldots \quad (18a)$$

Taking φ to be periodic with E_x, we have,

$$\varphi = \frac{p_y E_x (1 + f(\epsilon)/I}{F^2 - \omega^2 + i\omega G} \qquad \ldots \quad (21)$$

and, hence,
$$P_m = \Sigma N p_y \varphi = \frac{\Sigma N p_y^2 E_x (1 + f(\epsilon))/I}{F^2 - \omega^2 + i\omega G} \qquad \ldots \quad (22)$$

F^2, in these expressions, is given by,

$$F^2 = F_0^2 - \frac{4\pi}{3I}\Sigma N p_y^2.$$

The additional contribution to the dielectric constant would be $4\pi P_m/E_x$ and thus, we may write for the molecular part of the dielectric constant as,

$$K_m = \frac{4\pi(1 + f(\epsilon))\Sigma N_k p_y^2/I}{F^2 - \omega^2 + i\omega g}$$

The numerator, which is a constant depending upon the substance, is smaller than the numerator of the electric part by a factor of the order of 10^3, which is the approximate ratio of the molecular mass to the electronic mass. Thus the molecular polarisation will give rise to a small additional effect on the electronic effect and the calculated dielectric constant of a liquid medium,

on the basis of electronic polarisation only needs to be corrected by a very small amount. The form of the complete dielectric constant, would, thus, be given by,

$$K = 1 + 4\pi(P_e + P_m)/E_x$$

$$= 1 + \frac{4\pi\Sigma N_k e^2/m}{f_k^2 - \omega^2 + i\omega g} + \frac{4\pi\Sigma N_k p_y (1 + f(\epsilon))/I}{F^2 - \omega^2 + i\omega G} \quad \ldots (23)$$

The real part of the dieletric constant determines the value of $n^2 - k^2$, where n is the refractive index and k is the absorption coefficient. When we neglect k^2 compared to n^2, we may set,

$$n^2 = n_e^2 + \frac{4\pi C_m (F^2 - \omega^2)}{(F^2 - \omega^2)^2 + \omega^2 G^2}.$$

Here, n_e = the usual refractive index due to the electronic motion only, and

$$C_m = \Sigma N p_y^2 (1 + f(\epsilon))/I.$$

Considering the molecular contribution as the change in the usual value of $n_e^2 \simeq n^2$, obtained under the consideration of the electronic motion only, we have,

$$d(n^2) = 2ndn = \frac{4\pi C_m (F^2 - \omega^2)}{(F^2 - \omega^2)^2 + \omega^2 G^2}.$$

or

$$d\frac{C}{V} = \frac{CdA}{V^2} = n.\frac{dV}{V} = \frac{4\pi C_m/2n}{(F^2 - \omega^2) + \omega^2 g'^2}$$

or,

$$\frac{dV}{V} = \frac{2\pi C_m/n^2}{F^2 - \omega^2 + \omega^2 g'^2} \quad \ldots (24)$$

c, in the above equations denote the velocity of light in vacuum, and we have,

$$g'^2 = G^2/(F^2 - \omega^2).$$

The relation (24), above gives us the relative contribution of the molecular motion towards the optical wave velocity. When the coefficients F and G have a range and have a sufficiently large value to make its contribution effective in measurements of the velocity, we will have a broadening of the optical spectral lines due to internal dispersion. The broadening would be greater for substances with larger variability of the F and G values. In case, the F and G values are ineffective compared to ω^2, no such broadening of the lines will be expected. Further, it is expected, that although the rotational coefficients, treated in the optical case, might be of a completely different order from the corresponding coefficients treated in the elastic case, as they would involve the elastic preventive or polarising force, the range of variability, which depends on the molecular structure, would have a correspondence in the two cases, and would be guided by the Stokes' multiplier, M. Experiments with a plane diffraction grating show a broadening of the spectral lines corresponding

with the Stokes' multiplier M. This indicates the effectiveness of the coefficients compared to the value of ω^2. They are being reported in a separate paper (Mukherjee, 1952) in this issue (p. 154).

The imaginary part of the dielectic constant will give us the value of the absorption coefficient k, in two parts determined by the relation,

$$k = k\varepsilon + \frac{2\pi C_m \omega G}{n(F^2 - \omega^2)^2 + \omega^2 G^2}$$

From the experimental finding that there is an internal dispersion of the optical waves, it appears that the coefficients F and G are effective to some degree, and thus it is expected that there will be some measurable contributory part of the absorption coefficient due to molecular motion. A proper estimate of this, however, could not be made yet.

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REFERENCES

Bazulin, P., 1936, *C. R. Acad. Sci., U, R. S. S.*, **3**, 285
Biquard, P., 1935, These, Paris, also printed as 1936, *Ann. Phys. Paris.*, **6**, 195.
Debye, P., and Sears, F. W., 1932, *Proc. Nat. Acad. Sci.*, **18**, 410
Dutta, A. K., and Ghose, B. B., 1937-38, *Trans. Bose. Res. Inst.*, **13**, 31
Hunter, J. L , 1941, *J Accoust. Soc. Amer.*, **13**, 36.
Kneser, H. O., 1938, *Ann. der. Phys.*, **32**, 281.
Pinkerton, J M. M , 1948, *Nature*, 162, 106 ; 1949, *Proc. Phys. Soc.*, **62**, 129
Rapuano, R. A., 1947, *Phys. Rev.*, **72**, 78.
Slater, G. G., and Frank, N H., 1933, Theoretical Physics, *p.* 280.
Stokes, G G , 1845, *Trans. Camb. Phil. Soc* , **8**, 287.
Willard, G. W., 1941, *J. Accoust. Soc. Amer* , **12**, 438.